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Atomistic Simulations of a Thermotropic Biaxial Liquid Crystal

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We have performed molecular dynamics simulations of a 2,5-bis-(p-hydroxyphenyl)-1,3,4-oxadiazole mesogen (ODBP-Ph-C₇) at a fully atomistic level for a range of temperatures within the region that has experimentally been assigned to a biaxial nematic phase. Analysis of the data shows that the simulated nematic phase is biaxial but that the degree of biaxiality is small. The simulations show also the formation of ferroelectric domains in the nematic where the molecular short axis is aligned with the oxadiazole dipoles parallel to each other. Removal of electrostatic interactions leads to destabilization of ferroelectric domains and destabilization of the biaxiality. An additional simulation shows the slow growth of a mesophase directly from the isotropic fluid over a period of approximately 50 ns. This is the first time this has been achieved within the framework of an all-atom model.

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Predicted theoretically by Freiser more than 30 years ago [1], the phenomenon of nematic biaxiality has been observed in both lyotropic [2] and polymeric liquid crystals [3]. However, until recently biaxiality has remained elusive for thermotropic nematogens. A large variety of synthetic strategies have been employed to engineer new molecules, which could potentially exhibit orientational order along two perpendicular axes [4–7]. Although each strategy showed some merit, none of these succeeded in producing a verifiable biaxial phase. Recently this situation changed with both Madsen *et al.* [8] and Acharya *et al.* [9] reporting strong experimental evidence to have discovered the first biaxial phase in low molecular weight thermotropic liquid crystals based on molecules with an oxadiazole core (Fig. 1). These molecules are neither calamitic (rodlike) nor discotic (dislike) but belong to a third group of thermotropic mesogens known as bend-core mesogens [10]. Earlier theoretical work had predicted that bend-core systems could form mesophases [11]. However, the bend angle of the oxadiazole systems does not correspond to that predicted by theory, and at this stage it is not possible to attribute biaxial ordering in oxadiazole mesogens purely to molecular shape. It should also be noted that experiments to characterize the biaxial nematic phase further are not easy, since it is found to be stable only at high temperatures, which makes analysis difficult [8].

This Letter aims at analyzing the reported biaxial liquid crystalline phase of ODBP-Ph-C₇ (Fig. 1) using an atomistic simulation approach for the molecule and investigating the forces responsible for its formation. Simulation allows us to observe the evolution of the biaxial phase and study the structure of the phase itself at a molecular level.

Results are obtained from classical molecular dynamics simulations carried out with 256 molecules in a cubic simulation box at five state points corresponding to temperatures assigned experimentally to lie within the biaxial nematic region: 448, 458, 468, 478, and 488 K. The calculations use an all-atom molecular dynamics simula-

tion approach adopting the same methodology outlined in full in previous studies of the mesogen PCH5 [12,13]. In brief, the simulations used a harmonic force field of the OPLS-AA form obtained from a combination of *ab initio* quantum calculations to parametrize internal degrees of freedom and small molecule simulations to refine parameters for nonbonded terms [14,15]; employed partial electronic charges with an Ewald sum treatment of electrostatics; made use of the SHAKE procedure to constrain bond lengths with a time step of 2 fs; and were carried out in the constant-*NpT* ensemble using a Nosé-Hoover thermostat and a Hoover barostat coupled to a leap frog integrator. Simulations were started from an idealized perfectly aligned pseudonematic starting configuration with perfect order ($Q_{00}^2 = \langle S_2 \rangle \approx 1$, $Q_{22}^2 \approx 1$) at a gas phase density, compressed rapidly to liquid state density and equilibrated at a pressure of 1 bar. Additional simulations were started from an isotropic configuration with $Q_{00}^2 = \langle S_2 \rangle \approx 0$ at gas phase density. This was also compressed rapidly to liquid phase density and equilibrated to form an isotropic liquid phase.

The molecular orientation was calculated on the basis of three different criteria: (a) orthogonal vectors representing the three principal inertia axes of the molecule were obtained by diagonalizing the inertia tensor; (b) three orthogonal vectors were obtained from the central oxadiazole ring, with the ring long axis pointing along the nitrogen-nitrogen vector and the short axis pointing along

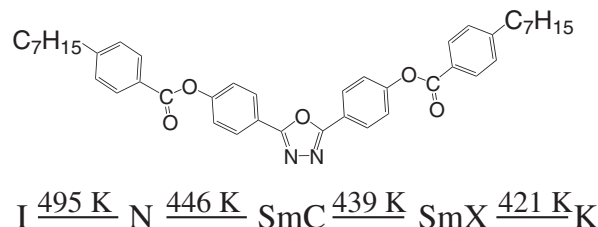


FIG. 1. Molecular structure and experimental transition temperatures of ODBP-Ph-C₇.

the vector from the center of the nitrogen-nitrogen bond to oxygen atom (generating a third vector from the cross product of the other axes); (c) three orthogonal vectors were obtained by calculating vectors running along the molecular arms and summing them to obtain a vector along the short axis of the molecule, then subtracting one arm vector from the other to obtain a long axis vector. Here we define the arm vectors in terms of (i) the oxidiazole ring only, (ii) the central oxidiazole ring plus secondary phenyl rings, (iii) the whole core plus chains. The results described below are found to be largely independent of which set of three vectors are used for analysis, indicating that biaxial ordering of the core is similar to that of the molecule as a whole. For brevity, results presented below are given only for set (a) and (c)(ii).

The director vectors, X , Y , and Z , for the three ordering directions of a system of biaxial molecules can be assigned to the eigenvectors obtained by diagonalizing three uniaxial ordering second rank tensors, $Q_{\alpha\beta}^{AA}$ [16] constructed from the three molecular axes ($A = X, Y, Z$) defined above. By convention, Z , is defined as the director parallel to the average direction of the long molecular axes and the uniaxial order parameter for the long axis, $\langle S_2^{ZZ} \rangle$ is given by

$$\langle S_2^{ZZ} \rangle = Q_{00}^2 = \langle ZQ^{zz}Z \rangle; \quad (1)$$

Y is taken as the short axes defined above and $\langle S_2^{YY} \rangle$ refers to the uniaxial order parameter for this axis. Following Allen [16] we also calculate the biaxial order parameter for the system using X , Y , and Z

$$Q_{22}^2 = \frac{1}{3} \langle XQ^{xx}X + YQ^{yy}Y - XQ^{yy}X - YQ^{xx}Y \rangle. \quad (2)$$

The order parameters for the system grown from a perfectly aligned nematic are shown in the top part of Fig. 2 for the midtemperature of 468 K. Here, loss of the initial perfect biaxial order occurs very rapidly within < 1.0 ns on cooling from the aligned gas to the nematic. However, considerably longer (> 6 ns) is allowed for the system to equilibrate. In Table I we give the mean values for each order parameter calculated from the final 3.5 ns of simulation for 5 temperatures. The system is seen to remain nematic and biaxial between 448 and 488 K, which covers the experimental range where biaxiality has been reported [8,9], with order parameters decreasing slightly as temperature is increased over this range. The measured biaxiality is small but sufficiently high to indicate a small degree of orientational order for the short axis within the phase. The fact that the values of $\langle S_2^{ZZ} \rangle$, $\langle S_2^{YY} \rangle$, and $\langle Q_{22}^2 \rangle$ do not depend significantly on the definition of the axes in Table I suggests that the biaxiality of the core is imposed on the molecule as a whole.

It should be stressed that the values for Q_{22}^2 are < 0.2 in all cases. Such values are smaller than expected from previous simulations of idealized models for biaxial molecules. For example, single site biaxial potentials, such as spheroids [16] and a biaxial Gay-Berne [17], predict a

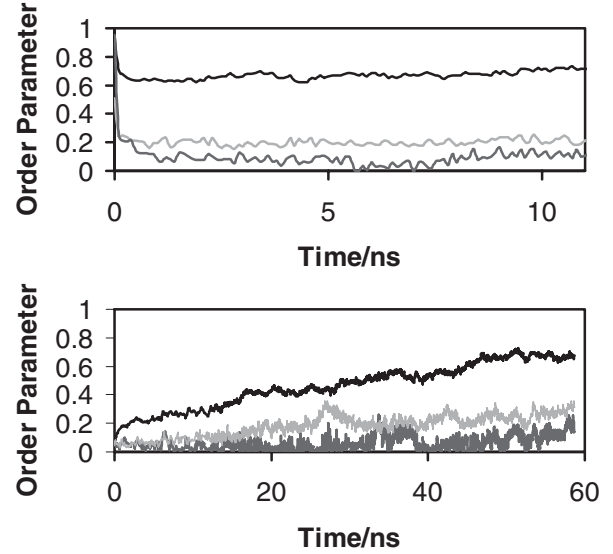


FIG. 2. Uniaxial order parameters calculated for the molecular long axis, $\langle S_2^{ZZ} \rangle$ (top line), short axis, $\langle S_2^{YY} \rangle$ (middle line), and biaxial order parameter $\langle Q_{22}^2 \rangle$ (bottom line) at 468 K. (a) Top graph—system grown from a perfectly aligned nematic; (b) system grown from the isotropic phase.

nematic range where the biaxial order parameter rises to > 0.6 and > 0.25 , respectively. In the case of the latter the biaxiality is limited by the onset of smectic ordering. For the current molecule a smaller degree of biaxiality is expected from the deuterium NMR results of Madsen *et al.* [8]. Also, for a limited system size of 256 molecules, we would expect some degree of system size dependence of the results, i.e., local biaxial fluctuations would be expected to contribute to $\langle S_2^{YY} \rangle$ and $\langle Q_{22}^2 \rangle$. We cannot test the extent of this effect by going to larger system sizes, as 256 molecules already represent an extremely large system to simulate over periods of > 10 ns. However, we are able to compare with values for these order parameters for a known uniaxial system: for 256 molecules of the uniaxial nematic mixture, E7, where the current authors have re-

TABLE I. Mean order parameters for a series of simulation temperatures. Values are calculated from using definition (a) and (c)(ii) for the three molecular axes. Values for (c)(ii) are included in parentheses.

Temperature/(K)	$\langle S_2^{ZZ} \rangle$	$\langle S_2^{YY} \rangle$	Q_{22}^2
448	0.73 ± 0.02 (0.70 ± 0.02)	0.27 ± 0.02 (0.27 ± 0.02)	0.11 ± 0.03 (0.10 ± 0.04)
458	0.74 ± 0.02 (0.71 ± 0.02)	0.23 ± 0.03 (0.23 ± 0.02)	0.08 ± 0.03 (0.07 ± 0.02)
468	0.71 ± 0.02 (0.68 ± 0.02)	0.24 ± 0.02 (0.24 ± 0.03)	0.12 ± 0.03 (0.10 ± 0.03)
478	0.68 ± 0.01 (0.66 ± 0.02)	0.22 ± 0.02 (0.22 ± 0.02)	0.09 ± 0.04 (0.10 ± 0.03)
488	0.65 ± 0.02 (0.62 ± 0.02)	0.22 ± 0.02 (0.22 ± 0.02)	0.09 ± 0.03 (0.08 ± 0.03)

cently performed atomistic simulations [18]. The value of $\langle S_2^{YY} \rangle = 0.2 \pm 0.02$ for E7 is comparable to that seen in this work, while the value of $\langle Q_{22}^2 \rangle = 0.06 \pm 0.03$ is clearly considerably less. Here, however, we can deduce that the relatively large value of $\langle S_2^{YY} \rangle$ for the E7 simulation is solely down to local biaxial fluctuations in a small system. For example, if we monitor the direction of the short-axis director in E7 we see quite rapid fluctuations in the direction of this vector. This contrasts with relatively slow diffusion of a well-defined short-axis director in ODBP-Ph-C₇.

Bates and Luckhurst [19] have suggested that an alternative way of quantifying the degree of biaxial ordering is by the biaxial parameter η . Here, $\eta = (q_{yy} - q_{xx})/q_{zz}$, where $|q_{zz}| > |q_{yy}| > |q_{xx}|$ for eigenvalues of the ordering tensor of a chosen axis. For ODBP-Ph-C₇, the ordering tensor for the long molecular (inertia) axes at 468 K yields a value of $\eta = 0.16 \pm 0.04$, whereas for E7 the value of η is 0.03 ± 0.02 . With this evidence, it seems quite clear that the orientational order in ODBP-Ph-C₇, although small, is fundamentally different to that in a uniaxial liquid crystal with local biaxial fluctuations. Madsen *et al.* [8] have measured a value of η in their NMR study by using quadrupolar splitting from a probe molecule of hexamethylbenzene dissolved in ODBP-Ph-C₇. In their work a value of η of 0.11 is measured. This measurement arises from the biaxial ordering of the probe molecule within the phase itself. We would expect a slightly higher phase biaxiality from the actual ODBP-Ph-C₇ molecules. As noted in [19], η values are expected to depend on the axis chosen within the molecule. In our work, larger values of η are available if other axes are chosen, e.g., a value of $\eta = 0.3 \pm 0.1$ is measured for the short axis at 468 K.

Turning to the interactions responsible for biaxiality, it has been suggested that the dipole across the center of the oxadiazole ring is important in stabilizing a biaxial phase. To this end it is interesting to note the formation of small ferroelectrically ordered domains in the sample. These are shown clearly in Fig. 3, where the color coding shows domains where the central dipoles are aligned. A more quantitative measure of this is provided by calculating the distance dependent pairwise dipole correlation function, $g_1(r) = \langle \cos\theta(r)_{ij} \rangle$, averaged over all molecular pairs i and j at a separation r for angles θ_{ij} between the short molecular axes (Fig. 4). Here, distances are measured relative to the center of the oxadiazole ring. The peak in $g_1(r)$ between ≈ 4.2 – 14.6 Å indicates a preference for a parallel arrangement of the core dipoles at these distances. [The sharp negative signal in $g_1(r)$ over a very small range of r at ≈ 3.3 Å occurs because two cores with parallel dipoles cannot approach this close without unfavorable steric repulsion.]

To test whether the small ferroelectric domains arise from preferential packing of the core or from electrostatics, we carried out additional simulations in which partial charges were removed from the system for further

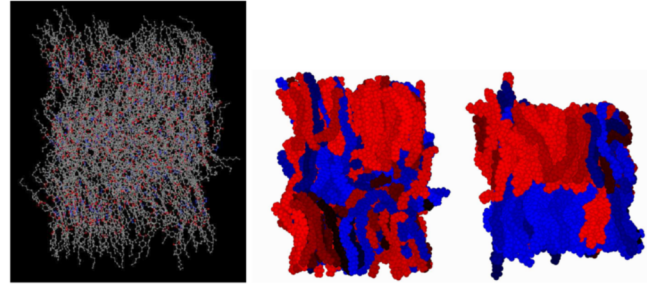


FIG. 3 (color online). Snapshot from a molecular dynamics simulation of the ODBP-Ph-C₇ at 468 K. Left: starting from a pseudonematic lattice after 11 ns of simulation time. Atoms and bonds are shown with hydrogens omitted for clarity. Middle: space filling color-coded representation of the same system. Colors show the orientation of the oxadiazole dipole across the short molecular axis of the core, with blue and red representing orientations at 180° degrees to each other. Bottom: ODBP-Ph-C₇ at 468 K starting from an isotropic starting configuration.

simulations at 468 K. The immediate influence of the removal of charges is a slight stabilization of the nematic phase, with the uniaxial order parameter from the long inertia axis increasing slightly to 0.8; accompanied by a decrease in $\langle Q_{22}^2 \rangle$ to 0.07 and a decrease in η for the long axis to 0.03. The change in density accompanying the removal of charges is very small $<0.1\%$ (from 1.049 to 1.048 g cm⁻³). As shown in Fig. 4 the reduction in biaxiality is associated with a destabilization of the ferroelectric domains. It therefore seems likely that ferroelectric parallel alignment of the cores helps in the stabilization of the biaxial nematic in ODBP-Ph-C₇. Possibly this is due to favorable quadrupolar stacking of the molecular cores. Reintroduction of the charges leads to a recovery of the original domains and order parameters over a 8 ns period.

In recent experimental work, Görtz and Goodby have reported that oxidiazole compounds can show interesting behavior with the formation of chiral domains of opposite handedness, as seen via optical microscopy [20]. We have therefore carried out extended simulations to study the

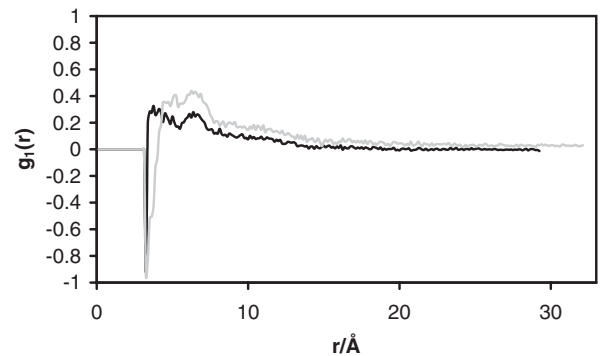


FIG. 4. The pairwise dipole correlation function, $g_1(r)$, calculated for short molecular axes at a temperature of 468 K. (Gray line—normal simulation. Bold line—simulation without charges).

behavior of ODBP-Ph-C₇ on cooling by taking an equilibrated isotropic liquid phase and quenching into the mesophase regime. The time evolution of the order parameters from this simulation is shown in Fig. 2. Here, growth of a liquid crystalline mesophase takes place over approximately 50 ns, (corresponding to approximately 12 CPU years on our parallel opteron computer system used for this work). To our knowledge this is the first time growth of a liquid crystal phase has been achieved for an all-atom liquid crystal model. The time scale for the orientational transition is very similar to that seen in the work of Berardi *et al.* who considered the orientational melting of a nematic to an isotropic phase close to the clearing point [21]; and is considerably longer than that required for united-atom [22] or coarse-grained simulation models [23]. The value of $\langle S_{zz}^2 \rangle$ at the end of the run are typical of those expected experimentally for a nematic system. Viewing the snapshot in Fig. 3 shows that the phase has formed into two distinct ferroelectric domains in quenching. For this simulation, both $\langle Q_{22}^2 \rangle$ and η are larger than seen in the earlier runs, respectively, 0.15 ± 0.05 and 0.29 ± 0.04 and these are clearly influenced by the size of the domains that are formed.

In Fig. 3 we note that the limited system size means that it is impossible to completely rule out formation of tilted smectic layers rather than nematic domains. However, the value of the order parameter is typical for a nematic, the system remains fluid with molecules moving and continually changing conformation, and there is no well-defined tilt direction within the domains, which we might expect if we had a tilted smectic. Görtz and Goodby suggested [20] that an achiral biaxial nematic can separate into two separate chiral domains. To test for this in the simulation results we have calculated the chirality for each molecule by means of the scaled chirality index, G_{05} [24]. Although individual molecular conformations are strongly chiral, the overall chirality cancels out through conformational averaging. Within the simulation error bars we can detect no difference in the chirality for the two domains formed. It should be stressed, of course, that the two domains seen here are limited by the size of the simulation box, $\approx (64 \text{ Å})^3$, which is very small compared to the domains seen experimentally.

Summary.—We have simulated the nematic phase of the molecule ODBP-Ph-C₇ at an all-atom simulation level for 256 molecules. The results show that the degree of biaxiality is small in this molecule as measured by the biaxial order parameter $\langle Q_{22}^2 \rangle$. However, we find that the biaxiality seen in this system is genuine and fundamentally different from the local biaxial fluctuations that arise in uniaxial systems. This is highlighted by comparisons of $\langle Q_{22}^2 \rangle$ and the phase biaxiality η from simulations of the uniaxial mixture, E7. The discovery of ferroelectric domains in this system is a surprising result. On removal of electronic charges these domains are destabilized, with a correspond-

ing drop in the biaxial order parameter but a rise in the uniaxial order of the long axis. The final simulations where two domains are grown during a quench from the isotropic liquid phase are the first to show the growth of a mesophase from an isotropic liquid for an all-atom model.

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- [1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
- [2] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
- [3] H. F. Leube and H. Finkelmann, Macro. Chem. Phys. **192**, 1317 (1991).
- [4] M. Lehmann and J. M. Levin, Mol. Cryst. Liq. Cryst. **411**, 1315 (2004).
- [5] J. Malthete, L. Liebert, A. M. Levelut, and Y. Galerne C.R. Acad. Sci. Ser. Gen., Ser. 2 **303**, 1073 (1986).
- [6] K. Praefcke, B. Kohne, B. Gundogan, D. Singer, D. Demus, S. Diele, G. Pelzl, and U. Bakowsky, Mol. Cryst. Liq. Cryst. **198**, 393 (1991).
- [7] I. D. Fletcher and G. R. Luckhurst, Liq. Cryst. **18**, 175 (1995).
- [8] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).
- [9] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).
- [10] G. Pelzl, S. Diele, and W. Weissflog, Adv. Mater. **11**, 707 (1999).
- [11] P. I. C. Teixeira, A. J. Masters, and B. M. Mulder, Mol. Cryst. Liq. Cryst. **323**, 167 (1998).
- [12] D. L. Cheung, S. J. Clark, and M. R. Wilson, Chem. Phys. Lett. **356**, 140 (2002).
- [13] D. L. Cheung, S. J. Clark, and M. R. Wilson, J. Chem. Phys. **121**, 9131 (2004).
- [14] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, J. Am. Chem. Soc. **118**, 11 225 (1996).
- [15] D. L. Cheung, S. J. Clark, and M. R. Wilson, Phys. Rev. E **65**, 051709 (2002).
- [16] M. P. Allen, Liq. Cryst. **8**, 499 (1990).
- [17] R. Berardi and C. Zannoni, J. Chem. Phys. **113**, 5971 (2000).
- [18] J. Peláez and M. R. Wilson (to be published).
- [19] M. A. Bates and G. R. Luckhurst, Phys. Rev. E **72**, 051702 (2005).
- [20] V. Görtz and J. W. Goodby, Chem. Commun. (Cambridge) 3262 (2005).
- [21] R. Berardi, L. Muccioli, and C. Zannoni, Chem. Phys. Chem. **5**, 104 (2004).
- [22] C. McBride, M. R. Wilson, and J. A. K. Howard, Mol. Phys. **93**, 955 (1998).
- [23] M. R. Wilson, Int. Rev. Phys. Chem. **24**, 421 (2005).
- [24] M. P. Neal, M. Solymosi, M. R. Wilson, and D. J. Earl, J. Chem. Phys. **119**, 3567 (2003).